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New Crystal-Growth Methods for Producing Lattice-Matched Substrates for High Temperature Semiconductors"

CRADA No. ORNL96-0420

Final Report

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PARTICIPANT : Commercial Crystal Laboratories (CCL), Naples, Florida

Project Summary:

This effort addressed the technical problem of identifying and growing, on a commercial scale, suitable single-crystal substrates for the subsequent deposition of epitaxial thin films of high temperature semiconductors such as GaN/AlN. The lack of suitable lattice-matched substrate materials was one of the major problem areas in the development of semiconducting devices for use at elevated temperatures as well as practical opto-electronic devices based on Al- and GaN technology. Such lattice-matched substrates are necessary in order to reduce or eliminate high concentrations of defects and dislocations in GaN/AlN and related epitaxial thin films. This effort concentrated, in particular, on the growth of single crystals of ZnO for substrate applications and it built on previous ORNL experience in the chemical vapor transport growth of large single crystals of zinc oxide. This combined expertise in the substrate growth area was further complemented by the ability of G. Eres and his collaborators to deposit thin films of GaN on the subject substrates and the overall ORNL capability for characterizing the quality of such films. The research effort consisted of research on the growth of two candidate substrate materials in conjunction with concurrent research on the growth and characterization of GaN films, i.e. the effort combined bulk crystal growth capabilities in the area of substrate production at both ORNL and the industrial partner, Commercial Crystal Growth Laboratories (CCL), Naples, Florida, with the novel thin-film deposition techniques previously developed in the ORNL SSD.

Project Background

The industrial partner, Commercial Crystal Laboratories, expressed a high level of interest in pursuing the subject CRADA activity in recognition of the existing and potential future demand for bulk substrate crystals for GaN growth as well as for the growth of related semiconductor thin films and superlattice structures. CCL had, in fact, previously developed a computer-controlled traveling furnace system particularized to the growth of bulk ZnO single crystals. In support of the CRADA activity, they moved this facility to ORNL and it was used in the CRADA effort as a portion of their in-kind contribution. The CRADA, as envisioned, represented an outstanding opportunity for combining the expertise of ORNL in ZnO growth and GaN film deposition with the expertise extant at CCL in the area of rutile and spinel growth in order to address a new research area that was important to several major DOE technologies and new initiatives. Additionally, due to the enormous commercial potential of the subject high-temperature semiconducting devices, success in carrying out the CRADA had the potential for resulting in follow-on funding and the corresponding commercialization of these materials.

Scientific & Technical Progress:

The chemical vapor transport crystal growth process was applied to the production of both pure and Sn-doped single crystals of ZnO. The addition of the Sn-dopant resulted in the growth of single crystals with increased electrical conductivity – a property that is desirable for some applications. These ZnO and Sn-doped ZnO single crystals formed the basis for a number of investigations of those properties of the materials that were relevant to their application to the growth of thin films as well as other applications. The crystal growth process that was refined and improved and the associated single-crystal samples that were produced are still adding value to ongoing DOE-supported research activities. During the ORNL/CCL ZnO crystal-growth CRADA, additional interest developed on the part of CCL in other ORNL-developed crystal-growth technologies. Specifically, CCL became interested in the ORNL work on the growth of single crystals of potassium tantalate and potassium tantalate niobate (KTN) – the later system representing an interesting electro-optic and photo-refractive material. This interest subsequently led to the development of an additional CRADA activity with CCL covering the growth of potassium tantalate niobate-based single-crystal substrates and the application of microwave processing to the improvement of the homogeneity of these materials. The advent of a successful major multi-year and multiple-investigator program by Eagle Picher Corp of Oklahoma resulted in their developing a commercially viable process for the growth of large single crystals of ZnO – a product that they successfully market and for which the market continues to expand to the present time. While significant progress was made in the course of the present subject small CRADA, the effort was not commensurate or, in the end, competitive with the large-scale project undertaken and funded by Eagle Picher. Nevertheless, due to the purity of the samples produced in the course of the subject CRADA, our single crystals continue to be used in carrying out both fundamental and applied investigations in DOE-supported projects both at ORNL and elsewhere.

Resulting Publications:

1. Olga Dulub, L. A. Boatner, and Ulrike Diebold, "STM Study of Cu growth on the ZnO surface," Surface Science Letters, (submitted for publication.)

2. F. A. Modine, L. A. Boatner, M. Bartkowiak, G. D. Mahan, H. Wang, and R. B. Dinwiddie, "Influence of Ceramic Microstructure on Varistor Electrical Properties," p. 469–491 in *Proceedings of the International Symposium on Dielectric Ceramic Materials,* Ceramic Transactions, Vol. **100** (American Ceramic Society, 1998).

3. Hsin Wang, Miroslaw Bartkowiak, Frank A. Modine, Ralph B. Dinwiddie, Lynn A. Boatner, and Gerald D. Mahan, "Nonuniform Heating in Zinc Oxide Varistors Studied by Infrared Imaging and Computer Simulation," *J. Am. Ceram. Soc.* **81**, (8) 2013–2022 (1998).

4. R. M. de la Cruz, R. Pareja, R. Gonzalez, L. A. Boatner, and Y. Chen, "Effect of Thermochemical Reduction on the Electrical, Optical-Absorption, and Positron-Annihilation Characteristics of ZnO Crystals," *Phys. Rev. B* **45**, (12) 6581–6586 (1992).

5. G. E. Jellison, Jr., and L. A. Boatner, “Optical Functions of Uniaxial ZnO Determined by Generalized Ellipsometry,” *Phys. Rev. B* **58**, (7) 3586–3589 (1998).